BIODIESEL PRODUCTION VIA SINGLE-STEP ALKALI CATALYST IN BATCH PROCESS

NURUL FARHA BINTI ABDUL RASHID

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Universiti Malaysia Pahang

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"I declared that this thesis entitled "Biodiesel Production via Single-Step Alkali Catalyst in Batch Process" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree."

Signature : .....

Name of Candidate : Nurul Farha Binti Abdul Rashid

Date : 14 May 2008

Special dedication to my beloved parents, Haji Abdul Rashid Bin Haji Abdullah P.J.K, Wan Rihana Binti Haji Wan Ahmad and all my lovely family members, Kakak, Wieyn, Wa, Ijat, Ira, Adik , and Daniel.

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ABSTRACT

Biodiesel is an alternative fuel, produced from domestic and renewable resources. Biodiesel is biodegradable, non-toxic, and essentially free of sulfur and aromatics. Biodiesel is made through a chemical process called transesterification whereby the glycerin, it's by product is separated from the fat or vegetable oil and sold to produce products such as soaps and grease. The main objective of this research is to produce the biodiesel from waste cooking oil and to optimize the production by using Design of Experiment (DOE). The single step alkali catalyzed process was adopted to prepare biodiesel by transesterification process by using the methanol and homogenous alkali catalyst, sodium hydroxide. The products was analyzed to determine the yield, concentration of methyl ester and moisture content to get the catalyst concentration and time at optimum condition by using DOE. From DOE it is found that the optimum condition to get the higher value of yield percentage was suggestion from RSM by the model equation is 56.31% with the reaction time is 30.37 minutes and catalyst concentration is 1.08%. For methyl ester concentration percentage, RSM suggested by the model equation is 77.96% with the reaction time is 30.24 minutes and catalyst concentration is 0.58%.

ABSTRAK

Biodiesel bermaksud bahan api alternatif yang diperolehi dari alam sekitar dan boleh diperbaharui. Biodiesel adalah mesra alam, tidak bertoksik dan mempunyai kandungan sulfur yang rendah. Biodiesel merupakan proses yang dihasilkan melalui proses kimia yang dipanggil transesterifikasi di mana gliserin, hasil sampingan dipisahkan dari minyak sayuran dan menghasilkan produk seperti sabun dan gris. Objektif utama untuk kajian ini adalah menghasilkan biodiesel daripada sisa minyak masak dan mengoptimumkan produk menggunakan Eksperimen Reka Bentuk (DOE). Proses pemangkin satu langkah telah diambil untuk menyediakan biodiesel dalam proses transesterifikasi dengan menggunakan metanol dan pemangkin alkali, natrium hidroksida. Hasil yang dapat (biodiesel) dianalisiskan untuk mengkaji peratus hasil, kepekatan metil ester dan kandungan air di dalam biodiesel untuk mendapatkan nilai kepekatan pemangkin dan masa tindak balas pada keadaan optimum dengan mengunakan Eksperimen Reka Bentuk (DOE). Dari keputusan DOE, keadaan optimum peratusan hasil yang dicadangkan oleh RSM melalui persamaan model adalah sebanyak 56.31% dengan kadar masa 30.37 minit dan kepekatan pemangkin sebanyak 1.08%. Manakala untuk kepekatan metil ester, RSM mencadangkan melalui persamaan model sebanyak 77.96% dengan kadar masa 30.24 minit dan kepekatan pemangkin sebanyak 0.58%.

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CHAPTER 1

INTRODUCTION

1.1 Overview of Research

Biodiesel is easy-to-make, clean burning diesel alternative made from vegetable oil or fats, and has great promise as an energy industry that could be locally-produced, used, and controlled. Biodiesel is an alternative fuel that is relatively safe and easy to process when conscientiously approached. It is made from vegetable oil or animal fat that can be used in any diesel engine without any modifications. Chemically, it is defined as the mono alkyl esters of long chain fatty acids derived from renewable lipid sources. It is thus distinguished from the straight vegetable oils (SVO) or waste vegetable oils (WVO) used as fuels in some diesel vehicles.

Biodiesel is biodegradable and non-toxic, and typically produces about 60% less net carbon dioxide emissions than petroleum-based diesel, as it is itself produced from atmospheric carbon dioxide via photosynthesis in plants. Biodiesel also produces fewer particulate matter, carbon monoxide, and sulfur dioxide emissions (all air pollutants under the Clean Air Act). Since biodiesel can be used in conventional diesel engines, the renewable fuel can directly replace petroleum products, reducing the country's dependence on imported oil.

Boasting an overall 92% reduction in toxic emissions compared to diesel, biodiesel is by far the best alternative fuel option at present. Biodiesel is the only alternative fuel currently available that has an overall positive life cycle energy balance. It is renewable, sustainable, and domestically produced. The only by-product of this form of biodiesel is glycerin, which can be easily used to make soap or other products. Biodiesel can also be produced from other biologically derived oils such as soybean oil, canola oil, sunflower oil, hemp oil, coconut oil, peanut oil, palm oil, corn oil, mustard oil, flaxseed oil, new or waste cooking oil, rapeseed oil, cottonseed oil, beef tallow, pork lard, as well as other types of animal fat.

In this research, biodiesel is produced through the reaction of the waste cooking oil with methanol in the presence of a catalyst to yield glycerin and biodiesel (chemically called methyl esters). The most common form uses methanol to produce methyl esters as it is the cheapest alcohol available, though ethanol can be used to produce an ethyl ester biodiesel and higher alcohols such as isopropanol and butanol have also been used. The use of waste cooking oil to produce biodiesel can reduce the raw material cost because it is estimated to be about half the price of virgin oil. The most common way to produce biodiesel is by transesterification process and the common catalyst used is homogeneous basic catalysts usually used a strong base such as potassium hydroxide. The alkali catalyzed process can achieve high purity and yield of biodiesel product in a short time.

1.2 Problem Statement

Biodiesel is needed for Malaysia future, toward the vision 2020. Since it's made domestically, it could reduce country’s dependence on foreign oil. At present, the high cost of biodiesel is the major obstacle to its commercialization. Biodiesel usually have high cost than petroleum-based diesel. The criteria of pollutants like unburned hydrocarbon, carbon monoxide, and particulate matter were increased with diesel fuel used. The problem with processing waste oils is that they usually contain large amounts of free fatty acids that cannot be converted to biodiesel using an alkaline catalyst due to formation of fatty acids salts (soap).

1.3 Objective of The Project

The main objective in this project is to produce the biodiesel from waste cooking oil by using alkali catalyst for replacement of diesel engine.

1.4 Scope of Research Work

The scopes of this research are to study the effect of catalyst concentration and reaction time at the optimum condition by using Design of Experiment (DOE) and to analyze the product by investigated the yield, methyl ester concentration content (TLC) and moisture content.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

"Bio" represents as a renewable and biological source in contrast to traditional petroleum-based diesel fuel; "diesel" refers to its use in diesel engines. As an alternative fuel, biodiesel can be used in neat form or mixed with petroleum-based diesel. Biodiesel defined as "a substitute for, or a additive to diesel fuel that is derived from the oils and fats of plants and animals" (Ma and Hanna, 1999) or mono-alkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetables oil or animal fat. Biodiesel is an alternative diesel fuel that is produced from vegetable oils and animal fats. It consists of the monoalkyl esters formed by a catalyzed reaction of the triglycerides in the oil or fat with a simple monohydric alcohol.

2.2 Biodiesel Production

Biodiesel production is the process of synthesizing biodiesel. Biodiesel is a liquid fuel source largely compatible with petroleum based diesel fuel. The most common method for its manufacture is synthesis by reacting glyceride-containing plant oil with a short chain alcohol such as methanol or ethanol in a step known as transesterification. The price of fossil diesel is soaring in these two years and it will be exhausted some day. Thus, looking for alterative way to develop a substitute for diesel

(biodiesel) is an imperious task for humans. Due to the increase in the price of the petroleum and the environmental concern about pollution coming from the car gases, biodiesel is becoming a developing area of high concern (Ma and Hanna, 1999).

Rudolph Diesel, a German engineer, introduced the diesel engine over a century ago (Nitske and Wilson, 1965). He tested vegetable oil as the fuel for his engine (Shay, 1993). Many researchers have concluded that vegetable oils and their derivatives hold promises as alternative fuels for diesel engines rather than spark-ignited engines due to their low volatility and high cetane number (Wagner et al., 1984, Scholl and Sorenson, 1993; Bagby et al., 1987). However, using raw vegetable oils for diesel engines can cause numerous engine-related problems (Korus et al., 1982; Perkins and Peterson, 1991). The increased viscosity and low volatility of vegetable oils lead to severe engine deposits, injector coking and piston ring sticking (Perkins and Peterson, 1991; Pestes and Stanislao, 1984; Clerk et al., 1984; Vellguth, 1983). However, these effects can be reduced or eliminated through transesterification of the vegetables oil to form alkyl ester (Perkins and Peterson, 1991; Zhang et al., 1988).

Vegetables oils, especially palm oil have become more attractive research recently because of their environmental benefits and the fact that it is made from renewable resources. Palm oils have the great potential for substitution of the petroleum distillates and petroleum based petrochemicals in the future. Others vegetable oil fuels are not now petroleum competitive fuels because they are more expensive than petroleum fuels (Demirbas, 2003). However, with the recent increase in petroleum prices and the uncertainties concerning petroleum availability, there is renewed interest in using vegetable oils in diesel engines. The diesel boiling range material is of particular interest because it has been shown to reduce particulate emissions significantly relative to petroleum diesel (Giannelos, Zannikos, Stournas, Lois, and Anastopoulos, 2002). There are more than 350 oil bearing crops identified, among which only palm oil, sunflower, safflower, soybean, cottonseed, rapeseed and peanut oils are considered as potential alternative fuels for diesel engines (Geoing, Schwab, Daugherty, Pryde, and Heakin, 1982).

From the viewpoint of chemical reaction, refined vegetable oil is the best starting material to produce biodiesel because the conversion of pure TG to FAME (fatty acid methyl ester) is high, and the reaction time is relatively short. Nevertheless, in China, the largest developing country with a population of over 1.3 billion, the limited refined edible oil must meet the need of consumers first. Waste cooking oil (WCO), if no suitable treatment is available, would be discharged and cause environmental pollution, but now, WCO is collected in Guangzhou, the third largest city in China, is over 20 thousand tons every year. This collected material is a good commercial choice to produce biodiesel due to its low cost (Wang et al, 2006).

Table 2.1: Physical and Chemical Properties of Biodiesel.

(American Standard Test Material, 2001)

Vegetable oil methyl ester	Kinematic viscosity (mm^2/s)	Cetane number	Lower heating value (MJ/l)	Cloud point (^oC)	Flash point (^oC)	Density (g/l)	Sulfur (wt %)
Peanut[a]	4.9 (37.8^{o}C)	54.00	33.60	5.00	176.00	0.88	-
Soybean[a]	4.5 (37.8^{o}C)	45.00	33.50	1.00	178.00	0.89	-
Soybean[b]	4.0 (40^{o}C)	45.7-56	32.70	-	-	0.880 (15^{o}C)	-
Babassu[a]	3.6 (37.8^{o}C)	63.00	31.80	4.00	127.00	0.88	-
Palm[a]	5.7 (37.8^{o}C)	62.00	33.50	13.00	164.00	0.88	-
Palm[b]	4.3-4.5 (40^{o}C)	64.3-70	32.40	-	-	0.872-0.877 (15^{o}C)	-
Sunflower[a]	4.6 (37.8^{o}C)	49.00	33.50	1.00	183.00	0.86	-
Tallow[a]	-	-	-	12.00	96.00	-	-
Rapeseed[b]	4.2 (40^{o}C)	51-59.7	32.80	-	-	0.882 (15^{o}C)	-
Used rapeseed[c]	9.48 (30^{o}C)	53.00	36.70	-	192.00	0.90	0.00
Used corn oil[c]	6.23 (30^{o}C)	63.90	42.30	-	166.00	0.88	0.00
Diesel fuel[b]	12-3.5 (40^{o}C)	51.00	35.50	-	-	0.830-0.840 (15^{o}C)	-
JIS-2D[c] **(Gas oil)**	2.8 (30^{o}C)	58.00	42.70	-	59.00	0.83	0.05

[a] Ref.10.
[b] Ref. 20.
[c] Ref. 19.

2.3 The Possible Methods of Biodiesel

The quality of feed vegetable oil particularly FFA content plays an important role in identifying the suitable technology. The important factors to be considered for a biodiesel production plant include:

i) Process ability of variety of vegetable oils without or minimum modifications
ii) Process ability of high free fatty acid (FFA) containing oils/feed-stocks
iii) Must be able to process raw both expelled and refined oil
iv) Process should be environment friendly with almost zero effluent

Certain difficulties are experienced in the engines while using straight vegetable oil (SVO) or chemically unmodified vegetable oils. One major problem is the higher viscosity of vegetable oils. The triglycerals as present in vegetable oil are mostly associated with their high viscosities, low volatilities and polyunsaturated character. Thus property modifications by transesterification are required to impart properties similar to petroleum diesel to the vegetable oil. The selection of appropriate technology for production of biodiesel calls for careful selection of processing steps, catalyst and downstream process integration.

There are the various methods for processing of biodiesel as follows:

i) Pyrolysis
ii) Micro-emulsification
iii) Trans-esterification

2.3.1 Pyrolysis

Pyrolysis refers to a chemical change caused by application of thermal energy in absence of air or nitrogen. The liquid fractions of the thermally decomposed vegetable oil are likely to approach diesel fuels. Many investigators have studied the pyrolysis of triglycerides with the aim of obtaining products suitable for diesel engines (Grossley *et al*, 1962; Schwab *et al*, 1988; Alencar *et al*, 1983; Billaud *et al*, 1995). Thermal decomposition of tri-glycerides produces compounds of several classes, including alkanes, alkenes, alkadienes, aromatics, and carboxylicacids. Different types of vegetable oils reveal large differences in composition when they are thermally decomposed. Pyrolyzed soybean oil, for instance, contains 79% carbon and 12% hydrogen (Dykstra *et al*, 1988). It also has low viscosity and a highcetane number compared to pure vegetable oils. However, while pyrolyzed vegetable oils possess acceptable amounts of sulphur, water, and sediment, as well as giving accept-able copper corrosion values, they are unacceptable in terms of ash, carbon residues, and pour point. In addition, though the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during thermal processing also eliminates any environmental benefits of using an oxygenated fuel (Ma and Hanna, 1999).

2.3.2 Microemulsification

The formation of micro-emulsions (co-solvency) is a potential solution for reducing the viscosity of vegetable oil. Micro-emulsions are defined as transparent, thermodynamically stable colloidal dispersions. The droplet in micro-emulsions ranges from 100 to 1000 Å. A micro-emulsion can be made of vegetable oils with an ester and dispersant (co-solvent), or of vegetable oils, an alcohol and a surfactant and a cetane improver, with or without diesel fuels. Water (from aqueous ethanol) may also be present in order to use lower-proof ethanol, thus increasing water tolerance of the micro-emulsions (Ziejewski, Kaufman, Schwab, and Pryde, 1984). The use of micro emulsions

with solvents such as methanol, ethanol, and 1-butanol has also been studied as a means of solving the problem of high viscosity of vegetable oils (Schwab, Bagby, and Freedman, 1987; Pryde, 1984; Ziejewski, Kaufman, Schwab,and Pryde, 1984). Micro emulsions are isotropic, clear or translucent thermodynamically stable dispersions of oil, water, a surfactant, and often a small amphiphilic molecule, called a co surfactant (Schwab, Bagby, and Freedman, 1987). Ziejewski *et al.* (Ziejewski, Kaufman, Schwab,and Pryde, 1984) prepared an emulsion of 53.3% (v/v) alkali-refined and winterized sunflower oil, 13.3% (v/v) 190-proof ethanol and 33.4% (v/v) 1-butanol. This non-ionic emulsion had a viscosity of 6.31 x 10^{-6} m^2/s at 40^oC, a cetane number of 25, a sulfur content of 0.01 %, free fatty acids of 0.01 %, and an ash content of less than 0.01%. Lower viscosities and better spray patterns were obtained by increasing the amount of 1-butanol. Schwab *et al.* (Schwab, Bagby, and Freedman, 1987) reported that 2-octanol was an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil. However, in a laboratory screening endurance test, irregular injector needle sticking, heavy carbon deposits, in complete combustion and an increase of lubricating oil viscosity were reported (Ziejewski, Kaufman, Schwab,and Pryde, 1984).

2.3.3 Transesterification

Transesterification also called alcoholysis which is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is employed instead of water. The other suitable alcohols include methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are utilized most frequently, especially methanol because of its low cost and its physical and chemical advantages. This process has been widely used to reduce the viscosity of triglycerides, thereby enhancing the physical properties of renewable fuels to improve engine performance (Clark, Wangner, S&rock, and Piennaar, 1984). Thus, fatty acid methyl esters (known as biodiesel fuel) obtained by transesteritication can be used as an alternative fuel for diesel engines. Transesterification is a chemical process of reacting

vegetable oils with alcohol in the presence of a catalyst as shown in Figure 2.1 where R1, R2, and R3 are long hydrocarbon chains, called fatty acid chains.

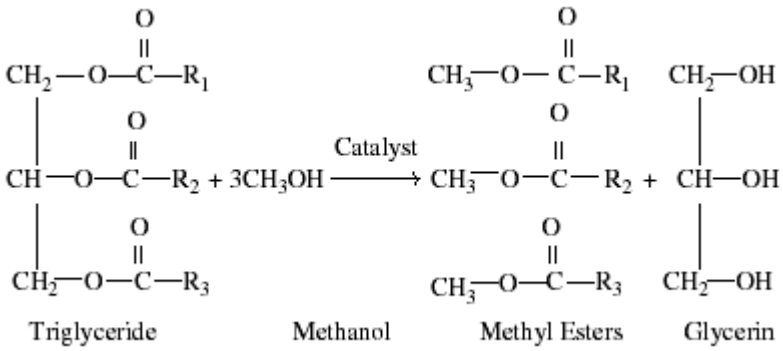


Figure 2.1: Transesterification of triglyceride using methanol and catalyst. (Zhang et al, 2002)

There are three basic routes to biodiesel production from biolipids (biological oils and fats):

i) Base catalyzed transesterification of the biolipid carried out under atmospheric pressure and at temperature ~60-70o C
ii) Direct acid catalyzed transesterification of the biolipid
iii) Conversion of the biolipid to its fatty acids and then to biodiesel

The overall process is normally a sequence of three consecutive steps, which are reversible reactions. In the first step, from triglycerides diglyceride is obtained, product of diglyceride monoglyceride and in the last step, from monoglycerides glycerin is obtained. In all these reactions esters are produced. The stoicheometric relation between alcohol and the oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product:

$$\text{Triglycerides (TG)} + \text{R}'\text{OH} \underset{k_2}{\overset{k_1}{\leftrightarrow}} \text{Diglycerides (DG)} + \text{R}'\text{COOR}_1,$$

$$\text{Diglycerides (DG)} + \text{R}'\text{OH} \underset{k_4}{\overset{k_3}{\leftrightarrow}} \text{Monoglycerides (MG)} + \text{R}'\text{COOR}_2,$$

$$\text{Monoglycerides (MG)} + \text{R}'\text{OH} \underset{k_6}{\overset{k_5}{\leftrightarrow}} \text{Glycerin (GL)} + \text{R}'\text{COOR}_3.$$

Figure 2.2: The reversible reactions between triglycerides and alcohol (Zhang et al, 2002)

2.4 The Transesterification Process of Biodiesel

The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters and glycerol. Methanol is the most commonly used alcohol due to its low cost (Ma and Hanna, 1999 and Demirbas, 2003). Transesterification significantly reduces the viscosity of vegetable oils without affecting the heating value of the original fuel. Therefore, fuel atomization, combustion, and emission characteristics will display better results than pure vegetable oils are used in engines. Many researchers around the world agree that biodiesel making from transesterification process, does not need to modify diesel engine before using the biodiesel. Scientists Duffy and Patrick conducted this process as early as 1853 (Metzer, 1996).

Methanol is the most commonly used alcohol because it's low cost. Other alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol and amyl alcohol. However, ethanol is a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment, however methanol is used because of its low cost and its physical and chemical advantages (Wang et al, 2006).

In general, a large excess of methanol is used to shift the equilibrium far to the right, so the reaction will not go back to the triglyceride anymore. Chemically, transesterification also called alcoholysis that means taking a triglyceride molecule or a complex fatty acid, neutralizing the free fatty acids, removing the glycerine and creating an alcohol ester. The function of catalyst is usually used to improve the reaction rate and yield. Alcohols are primary or secondary monohydric aliphatic alcohols having 1-8 carbon atoms (Sprules, Price, 1950).

2.5 Reaction Mechanism of Biodiesel Production

The reaction mixture settles and separates into an ester phase and a glycerol phase. The ester phase contains glycerides, methyl esters and methanol which are purified by distillation to obtain the final biodiesel. The remaining unreacted glycerides are reintroduced in the transesterification reactor together with traces of esters which allow for a better mixture of the alcohol and oil phases. The glycerol phase which contains glycerol, water and methanol, is fed into a buffer tank which also contains the glycerol phase from the transesterification reactor. Once the two glycerol phases are well mixed, they are fed into an acidulation tank where FFA from the pre-esterification are added until having an alkaline pH to avoid the formation of soaps and emulsions. The remaining unreacted FFA is sent again into a FFA buffer tank to be reused in the preesterification reactor. The glycerol phase is neutralized and distilled to recuperate glycerol and methanol to be reused within the system. By this process, the transesterification takes place at moderate conditions and the biodiesel conversion reaches its highest rate, above 95% (Mittelbach, 2004).

During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline (NaOH, KOH or sodium silicate). The main reason this process to produce biodiesel, is to find out how much alkaline is needed to ensure a complete transesterification. The alcohol reacts with the fatty acids to form

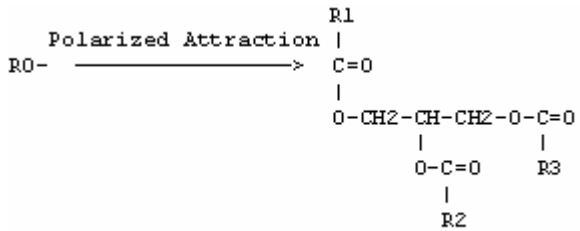
the mono-alkyl ester (or biodiesel) and crude glycerol. The reaction between the biolipid (fat or oil) and the alcohol is a reversible reaction so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion (Freedman et., 1984).

2.5.1 Base Catalyzed Mechanism

Base catalyzed reaction uses strong base such as NaOH, KOH, Sodium Methoxide and others. The base is dissolved in the alcohol to disperse solid catalyst into the oil. Any water in the process promotes the saponification reaction and inhibits the transesterification reaction.

The reaction equilibrium is far to the left. While KOH and NaOH are strong bases, such as methoxide can only be produced by reacting sodium metal in alcohol. However, the following reaction mechanism using methoxide as an example is common in the literature as methoxide is an excellent base catalyst for this reaction.

Once the alcohol mixture is made, it is added to the triglyceride. The reaction that follows replaces the alkyl group on the triglyceride in a series of reactions. The carbon on the ester of the triglyceride has a slight positive charge, and the oxygen have a slight negative charge, most of which is located on the oxygen in the double bond. This charge is what attracts the RO^- to the reaction site.



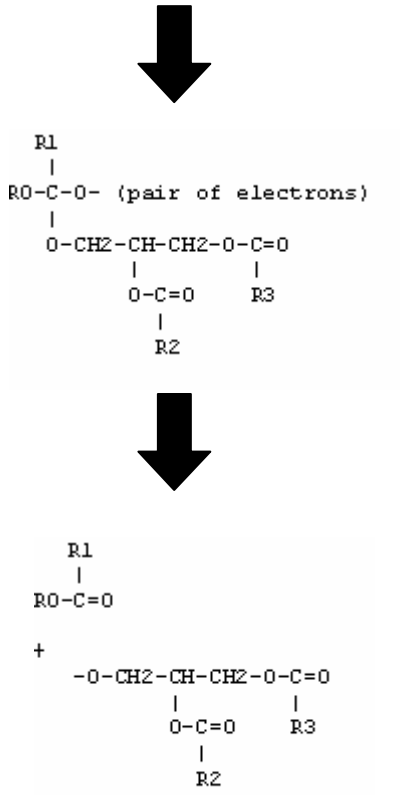


Figure 2.3: The reaction mechanism by using strong base catalyst

This yields a transition state that has a pair of electrons from the C=O bond now located on the oxygen that was in the C=O bond. These electrons then fall back to the carbon and push off the glycol forming the ester. Then two more RO groups react via this mechanism at the other two C=O groups. This type of reaction has several limiting factors. RO^- has to fit in the space where there is a slight positive charge on the C=O. So MeO- works well because it is small.

As the R on RO- gets bigger, reaction rates decrease. This effect is called steric hindrance. That is why methanol and ethanol are typically used. There are several competing reactions, so care must be taken to ensure the desired reaction pathway occurs. Most methods do this by using an excess of RO^-. The acid catalyzed method is a slight variant that is also affected by steric hindrance.

2.6 Transesterification Catalysis

The transesterification reaction can be catalyzed by alkali, acids or enzymes. The first two types have received the greatest attention and are the focus of many of the researchers. As for the enzyme-catalyzed system, it is requires a much longer reaction time than the other two systems (Nelson et al., 1996; Watanabe et al., 2001).

Chemically catalyzed processes, including alkali catalyzed and acid catalyzed ones have proved to be more practical nowadays. An alkali catalyzed process can achieve high purity and yield of biodiesel product in a short time (30-60min) (Muniyappa et al., 1996; Antolin et al., 2002). However, it is very sensitive to the purity of the reactants. Only well refined vegetable oil with less than 0.5 wt% of free fatty acid (FFA) can be used as the reactants in this process (Zhang, Dube, McLean, 2003). The most commonly preferred acid catalyst is sulfuric, sulphonic and hydrochloric acids. Sodium hydroxide, sodium methoxide and potassium hydroxide are preferred as alkaline catalyst. For transesterification reactions the concentration of catalyst ranges from 0.5 to 1.5 wt% (Freedman et., 1984).

2.6.1 Acid-Catalyzed or *In-Situ* Transesterification

Acids used for transesterification include sulfuric, phosphoric, hydrochloric, and organic sulfonic acids. Although transesterification by acid catalysts is much slower than that alkali catalysis (Ma and Hanna; Srivastava and Prasad; and Freedman et al., 1984), acid-catalyzed transesterification is more suitable for glycerides that have relatively high free fatty acid contents and more water (Freedman et al., 1984; Aksoy et al, 1988).

In situ transesterification differs from the conventional reaction in that the oil-bearing material contacts acidified alcohol directly instead of reacting with purified oil and alcohol. In the transesterification of waste cooking oil with acidified methanol produces fatty acid methyl ester is produced significantly greater than those obtained from the conventional reaction (Harrington and D'Arcy-Evans, 1985).

2.6.2 Enzymatic Transesterification by Lipase

Both extracellular and intracellular lipases are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems. In particular, it should be noted that the by-product, glycerol, can be easily recovered without any complex process, and also that free fatty acids contained in waste oils and fats can be completely converted to methyl esters. On the other hand, in general the production cost of a lipase catalyst is significantly greater that of an alkali one.

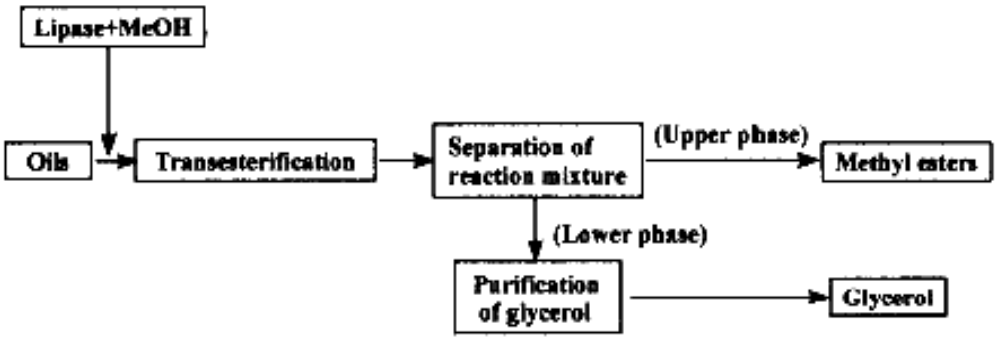


Figure 2.4: Flow diagram biodiesel production using the lipase catalyst. (Fukuda et al, 2001)

2.6.3 Alkali-Catalyzed Transesterification

Alkali used for transesterification includes NaOH, KOH, carbonates, and alkoxides such as sodium methoxide, sodium propoxide, and sodium butoxide. Alkali-catalyzed transesterification proceeds approximately 4000 times faster than that catalyzed by the same amount of an acidic catalyst (Formo, M.W, 1954), and is thus most often used commercially.

Table 2.2: Effect of the catalyst on the biodiesel purity and yield (G. Vicente et al , 2004)

Catalyst				
	Sodium hydroxide	**Potassium hydroxide**	**Sodium methoxide**	**Potassium methoxide**
Biodiesel purity (wt%)	99.7	99.69	99.7	99.4
	99.75	99.8	99.69	99.5
	99.72	99.8	99.72	99.65
	99.65	99.74	99.75	99.53
	99.71 ±0.04	99.76 ± 0.05	99.72 ± 0.03	99.52 ± 0.1
Biodiesel yield (wt%)	86.33	91.67	99.17	98.33
	86.67	91.67	99.33	98.5
	87	91.33	99.83	98.33
	86.71	92	99	98.67
	86.71± 0.28	91.67 ± 0.27	99.33 ± 0.36	98.46 ± 0.16

Temperature = 65 °C, molar ratio = 6, catalyst = 1%

2.6.3.1 Effects of Moisture and Free Fatty Acids

For alkali-catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous because water causes a partial reaction change to saponification, which produces the soap (Wright et al., 1944). The soap consumes the catalyst and reduces the catalytic efficiency, as well as causing an increase in viscosity, the formation of gels, and difficulty in achieving separation glycerol. (Ma *et al*., 1998) suggested that the free fatty acid content of the refined oil should be as low as possible, below 0.5%, and Feuge and Grose (Feuge and Grose, 1949) also stressed the importance of oils being dry and free of free fatty acids. Freedman *et al.* (Freedman, Pryde, and Mounts, 1984) reported that the products were significantly reduced if the reactants did not meet these requirements; sodium hydroxide or sodium methoxide reacted with moisture and carbon dioxide in the air, diminishing their effectiveness.

2.6.3.2 Effect of Molar Ratio of Alcohol to Vegetable Oil (WCO)

Another important variable affecting the ester yield is the molar ratio of alcohol to waste cooking oil. The stoichiometry of the transesterification reaction requires 3 mol alcohol per mol of triglyceride to yield 3 mol of fatty esters and 1 mol glycerol (see Fig.1). Higher molar ratios result in greater ester conversion in a shorter time. Freedman *et al.* (Freedman, Pryde, and Mounts, 1984) studied the effect of molar ratios (from 1:1 to 6:1) on ester conversion with vegetable oils. Soybean, palm, sunflower, peanut and cotton seed oils behaved similarly, with the highest conversion being achieved at a 6:1 molar ratio. Thus, a molar ration of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% on a weight basis (Feuge and Grose, 1949; Fillieres et al., 1995).

2.6.3.3 Effect of Catalyst Type

Sodium methoxide has been found to be more effective than sodium hydroxide, presumably because a small amount of water is produced upon mixing NaOH and MeOH (Freedman, Pryde, and Mounts, 1984; and Hartman, 1956). Alcantara *et al.* (Alcantara, Amores, Canoira, Fidalgo, France, and Navarro, 2000) transformed three fatty materials- bean oil, used frying oil, and tallow- with sodium methoxide into two different types of products by transesterification and amidation reaction with methanol and diethylamine, respectively. Amides enhance the ignition properties of petrochemical diesel fuel. However, sodium hydroxide and potassium hydroxide (Nye et al., 1983) are also able to catalyze transesterification, and because of their low cost, are widely used in industrial biodiesel production.

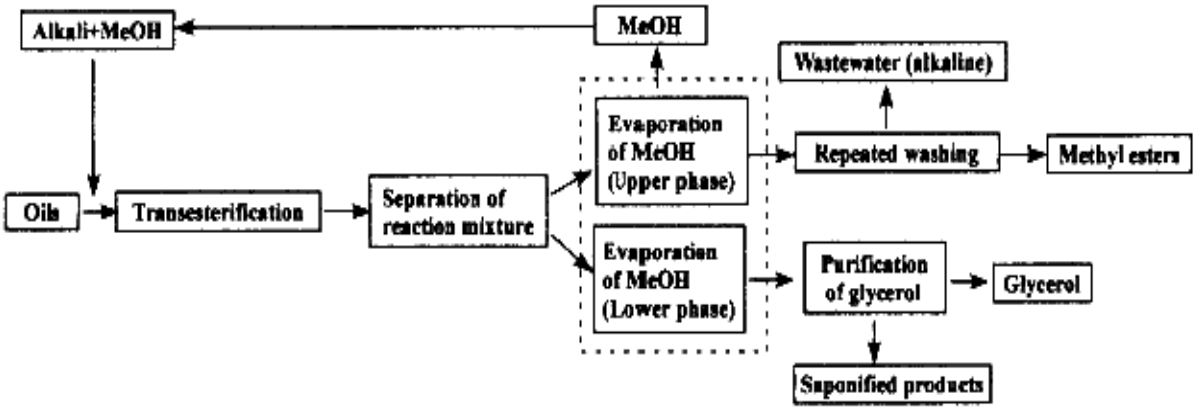


Figure 2.5: Flow diagram biodiesel production using the alkali catalyst. (Fukuda et al, 2001)

Table 2.3: The comparison of method between alkali-catalysis, lipase-catalysis and acid-catalysis for biodiesel production.

(Marchetti *et al*., 2007)

	Alkali-catalysis process	**Lipase-catalysis process**	**Acid-catalysis process**
Reaction temperature	60-70^{o}C	30-40^{o}C	55-80^{o}C
Free fatty acids in raw material	Saponified products	Methyl esters	Esters
Water in raw materials	Interference with the reaction	No influence	Interference with the reaction
Yield of methyl esters	Normal	Higher	Normal
Recovery of glycerol	Difficult	Easy	Difficult
Purification of methyl esters	Repeated washing	None	Repeated washing
Production cost of catalyst	Cheap	Relatively expensive	Cheap

2.7 The Advantages of Biodiesel

Biodiesel production is a very modern and technological area for researchers due to the relevance that it is winning everyday because of the increase in the petroleum price and the environmental advantages.

Although biodiesel cannot entirely replace petroleum-based diesel fuel, there are at least five reasons that justify its development, such as provides a market for excess production of vegetable oils and animal fats, decreases the country's dependence on imported petroleum although will not eliminate. Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. A life cycle analysis of biodiesel showed that overall CO_2 emissions were reduced by 78% compared with petroleum-based diesel fuel (Sheehan, Camobreco, Duffield, Graboski, and Shapouri, 1998). The exhaust emissions of carbon monoxide, unburned hydrocarbons, and particulate emissions from biodiesel are lower than with regular diesel fuel. Unfortunately, most emissions tests have shown a slight increase in oxides of nitrogen (NO_2). When added to regular diesel fuel in an amount equal to 1–2%, it can convert fuel with poor lubricating properties, such as modern ultra-low-sulfur diesel fuel, into an acceptable fuel (Canakci, Van Gerpen, 2001).

2.8 The Comparison between Biodiesel and Diesel Fuel

There are a number of ways in which a comparison between conventional fuels and biodiesel can be made. For overall ozone forming potential of biodiesel is less than diesel fuel. The ozone forming potential of the speculated hydrocarbon emissions was nearly 50 percent less than that measured for diesel fuel (Bala BK., 2005). Sulfur emissions are essentially eliminated with pure biodiesel. The exhaust emissions of sulfur oxides and sulfates from biodiesel were essentially eliminated compared to sulfur oxides and sulfates from diesel. Criteria pollutants are reduced with biodiesel use. The use of

biodiesel in an unmodified Cummins N14 diesel engine resulted in substantial reductions of unburned hydrocarbons, carbon monoxide, and particulate matter. Emissions of nitrogen oxides however were slightly increased. The exhaust emissions of carbon monoxide from biodiesel were 50 percent lower than carbon monoxide emissions from diesel (A. Demirbas, 2003). Breathing particulate has been shown to be a human health hazard. The exhaust emissions of particulate matter from biodiesel were 30 percent lower than overall particulate matter emissions from diesel. The exhaust emissions of total hydrocarbons were 93 percent lower for biodiesel than diesel fuel (Bala BK., 2005). NO_2 emissions from pure (100%) biodiesel increased in this test by 13 percent. However, biodiesel's lack of sulfur allows the use of NO_2 control technologies that cannot be used with conventional diesel. So, biodiesel NO_2 emissions can be effectively managed and efficiently eliminated as a concern of the fuel's use.

Biodiesel degrades about four times faster than petroleum diesel. Within 28 days, pure biodiesel degrades 85 to 88 percent in water (Korbitz.W, 1999). The flash point of a fuel is defined as the temperature at which it will ignite when exposed to a spark or flame. Biodiesel's flash point is over 300 deg. Fahrenheit, well above petroleum based diesel fuel's flash point of around 125 deg. Fahrenheit. Testing has shown the flash point of biodiesel blends increases as the percentage of biodiesel increases. Therefore, biodiesel and blends of biodiesel with petroleum diesel are safer to store, handle, and use than conventional diesel fuel (Korbitz.W, 1999)